

## Silicon single crystal wafer and method for producing silicon single crystal wafer

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### Abstract

There is disclosed a silicon single crystal wafer produced by processing a silicon single crystal ingot grown by Czochralski method with doping nitrogen, characterized in that a size of grown-in defects in the silicon single crystal wafer is 70 nm or less, a silicon single crystal wafer produced by processing a silicon single crystal ingot grown by Czochralski method with doping nitrogen, the silicon single crystal ingot is grown with controlling a rate of cooling from 1150 to 1080 DEG C to be 2.3 DEG C/min or more, and a method for producing a silicon single crystal wafer wherein a silicon single crystal ingot is grown with doping nitrogen and controlling a rate of cooling from 1150 to 1080 DEG C to be 2.3 DEG C/min or more, and is then processed to provide a silicon single crystal wafer. The silicon single crystal wafer for device wherein growth of the crystal defects is suppressed can be produced by CZ method in high productivity.

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[0009] Preferably, in the silicon single crystal wafer produced by processing a silicon single crystal ingot grown by Czochralski method with doping nitrogen, the silicon single crystal ingot is grown with controlling a rate of cooling from 1150 to 1080 DEG C to be 2.3 DEG C/min or more.

[0010] As described above, in the silicon single crystal wafer produced by processing a silicon single crystal ingot grown by CZ method with doping nitrogen, grown-in defects present on the wafer is very few due to presence of doped nitrogen. When the crystal ingot is grown with controlling the rate of cooling from 1150 DEG C to 1080 DEG C at 2.3 DEG C/min or more, the size of the crystal defects can be extremely decreased to have almost no harmful influence on fabrication of the device. Furthermore, since growth of crystal defects can be suppressed, it is possible to grow crystal at high speed, so that productivity can also be improved.

[0011] In the above case, the nitrogen concentration in the above-mentioned silicon single crystal wafer is preferably in the range of  $0.2$  to  $5 \times 10^{15}$  atoms/cm<sup>3</sup>.

[0012] In order to suppress growth of crystal defect, the nitrogen concentration is preferably  $1 \times 10^{10}$  atoms/cm<sup>3</sup> or more. In order not to prevent crystallization of single crystal, the nitrogen concentration is preferably  $5 \times 10^{15}$  atoms/cm<sup>3</sup> or less. However, the nitrogen concentration in the range of  $0.2$  to  $5 \times 10^{15}$  atoms/cm<sup>3</sup> is the most effective for suppression of growth of crystal defects, and therefore growth of crystal defects can be sufficiently suppressed when the nitrogen concentration is in the range.

[0013] During growth of the silicon single crystal ingot by Czochralski method with doping nitrogen, a concentration of oxygen in the single crystal ingot is preferably controlled to be  $1.0 \times 10^{18}$  atoms/cm<sup>3</sup> (ASTM '79 value) or less. When the oxygen concentration is low as above, growth of the crystal defects can be further suppressed, and formation of oxide precipitates in the surface layer can be prevented.

[0014] A silicon single crystal wafer as described above has very few crystal defects on the surface. Particularly, since the density of the crystal defects can be decreased to 40 number/cm<sup>2</sup> or less, yield can be improved significantly in fabrication of the device so that productivity of the crystal can be significantly improved.

[0015] The present invention also provides a method for producing a silicon single crystal wafer wherein a silicon single crystal ingot is grown with doping nitrogen and controlling a rate of cooling from 1150 to 1080 DEG C to be 2.3 DEG C/min or more, and is then processed to provide a silicon single crystal wafer.

[0016] As described above, in CZ method for growing a silicon single crystal ingot, growth of crystal defects incorporated during growth of crystal can be suppressed by doping nitrogen. Furthermore, since growth of crystal defects can be suppressed by growing crystal with controlling a rate of cooling from 1150 to 1080 DEG C to be 2.3 DEG C/min or more, crystal defects become very fine. Since growth of the crystal defects can be significantly suppressed, crystal can be grown at high speed, so that productivity of the crystal can be significantly improved.

[0017] The nitrogen concentration doped in the single crystal ingot is preferably  $0.2$  to  $5 \times 10^{15}$  atoms/cm<sup>3</sup>. The concentration of oxygen in the single crystal ingot is preferably  $1.0 \times 10^{18}$  atoms/cm<sup>3</sup> or less.

[0018] As described above, when cooling is performed at high speed and the concentration of doped nitrogen and the concentration of oxygen are controlled to be in the optimum range in production of silicon single crystal by CZ method with doping nitrogen, the silicon single crystal wafer having high quality and few crystal defects can be produced in high productivity.

[0019] In the silicon single crystal wafer produced by processing a silicon single crystal ingot grown by Czochralski method with doping nitrogen, a size of grown-in defects in the silicon single crystal wafer can be 70 nm or less, and thus yield and quality of the device can be improved.

[0020] According to a method for producing a silicon single crystal wafer of the present invention, a silicon single crystal ingot is grown with doping nitrogen and with controlling a rate of cooling from 1150 to 1080 DEG C to be 2.3 DEG C/min or more, and is then processed to provide a silicon single crystal wafer. Therefore, it is possible to suppress growth of the crystal defects in the silicon single crystal produced by CZ method, and to produce the silicon single crystal wafer wherein crystal defects detected in the surface layer of the wafer are very small, and the number of crystal defects are very small, easily and in high productivity.

## BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a graph showing a relation between a size of grown-in defect and the number of defects having the size in the silicon single crystal wafer in which nitrogen is doped.

Fig. 2 is a graph showing a relation between a size of grown-in defect and the number of defects having the size in the silicon single crystal wafer in which nitrogen is not doped.

Fig. 3 is a graph showing a relation between an average value of crystal defect density of the silicon single crystal wafer sliced from the five silicon single crystal ingots in which nitrogen is doped and a rate of cooling.

Fig. 4 is a graph showing the defect density of the silicon single crystal wafer obtained from the ingot grown with doping nitrogen and with controlling a rate of cooling to be 2.3 DEG C/min.

Fig. 5 is a graph showing the defect density of the silicon single crystal wafer obtained from the ingot grown without doping nitrogen.

## DESCRIPTION OF THE INVENTION AND EMBODIMENT

[0022] The present invention will now be described in more detail. However, the invention is not limited thereto.

[0023] The inventors have found that the size of crystal defects significantly depends on a rate of cooling crystal from 1150 to 1080 DEG C as a crystal producing condition in addition to doping of nitrogen during growth of silicon single crystal by CZ method, and that there can be obtained a silicon single crystal wafer wherein the crystal defects in a device fabricating layer (the surface layer of the wafer) are fine enough to cause no matter as a result of suppression of growth of crystal defects due to aggregation or the like, by controlling the rate of cooling to be high as 2.3 DEG C/min or more, and have accomplished the present invention by studying the conditions.

[0024] Namely, it is reported that agglomeration of vacancies in the silicon is suppressed when nitrogen is doped in a silicon single crystal so that density of a crystal defect is decreased (T. Abe and H. Takeno, Mat. Res. Soc. Symp. Proc. Vol. 262, 3, 1992). It is considered that the effect can be achieved with a result that vacancy agglomeration process is transited from homogenous nuclei formation to heterogeneous nuclei formation. Accordingly, the silicon single crystal having very small crystal defect can be obtained by growing a silicon single crystal by CZ method with doping nitrogen, and thus the silicon single crystal wafer having very small crystal defect can be obtained by processing it. According to the method, it is not always necessary to decrease growth rate of crystal, not as in the conventional method, and thus a silicon single crystal wafer having low defects density can be produced in high productivity.

[0025] Furthermore, the size of crystal defects significantly depends on time of passing in aggregation temperature range of vacancies. It is known that the aggregation temperature range of vacancies is 1150 to 1080 DEG C, and thus it can be predicted that the size of crystal defects can be decreased by shortening the time of passing in the temperature range when the crystal is grown. Accordingly, in the present invention, the crystal is grown with controlling a rate of cooling from 1150 DEG C to 1080 DEG C, which is the range of aggregation temperature, to be 2.3 DEG C/min or more, preferably 3.5 DEG C/min or more. It is thereby possible to shortening time of passing in an aggregation temperature range, so that the size of crystal defects can be decreased to be fine so as to cause no matter in fabrication of a device.

[0026] The reason why growth of crystal defect generated in silicon can be suppressed by doping nitrogen in silicon single crystal is, as described above, considered to be that vacancy agglomeration process is transited from homogenous nuclei formation to heterogeneous nuclei formation.

[0027] Accordingly, the concentration of doped nitrogen is preferably  $1 \times 10^{10}$  atoms/cm<sup>3</sup> or more, at which heterogeneous nuclei formation can be caused sufficiently. When it is more than  $5 \times 10^{15}$  atoms/cm<sup>3</sup>, which is solid solubility of nitrogen in silicon single crystal, crystallization of single crystal is inhibited. Therefore, it is preferably not more than the concentration.

[0028] Furthermore, the inventors of the present invention have further studied the concentration of nitrogen, and found that the most effective nitrogen concentration is in the range of  $0.2$  to  $5.0 \times 10^{15}$  atoms/cm<sup>3</sup>. When the concentration of doped nitrogen is relatively high as the above range, the highest effect of suppressing formation of crystal defects by doping nitrogen can be achieved, and formation of large crystal defect which may cause problem can be prevented almost completely.

[0029] On the other hand, it is known that a nitrogen atom in a silicon single crystal accelerates oxygen precipitation during the growth of the crystal (for example, in F. Shimura and R. S. Hockett, Appl. Phys. Lett. 48, 224, 1986). Accordingly, when the single crystal having general concentration at oxygen ( $1 \times 10^{18}$  atoms/cm<sup>3</sup> or more) is used, it may form oxide precipitate which is harmful to the device forming

## (Example, Comparative Example)

[0041] In accordance with CZ method, 40 kg of polycrystalline material of silicon was charged into a quartz crucible having a diameter of 18 inches, six single crystal ingots of silicon having a diameter of 6 inches P conductive type and orientation &lang100&rang were pulled, at a pulling rate of 1.2 mm/min as usual value.

[0042] Five of them were pulled while silicon wafer having silicon nitride film is previously charged into the silicon melt so that nitrogen concentration in the crystal of  $0.2$  to  $5.0 \times 10^{15}$  atom/cm<sup>3</sup> can be achieved. The number of rotation of the crucible was controlled so that the low concentration of oxygen in the single crystal of  $0.8$  to  $1.0 \times 10^{18}$  atoms/cm<sup>3</sup> can be achieved. Each of the single crystal ingot was pulled with controlling a rate of cooling from  $1150$  to  $1080$  DEG C through use of a cooling apparatus provided in a chamber of a CZ method silicon single crystal growing apparatus to be  $1.2$ ,  $1.6$ ,  $2.3$ ,  $3.0$ ,  $3.5$  DEG C/min.

[0043] Another crystal ingot was pulled without doping nitrogen in accordance with a conventional method. The crystal ingot was pulled with controlling a rate of cooling from  $1150$  to  $1080$  DEG C to be  $2.3$  DEG C/min. The concentration of oxygen in the single crystal was controlled to be  $0.8 \times 10^{18}$  atoms/cm<sup>3</sup>.

[0044] The wafers were sliced with a wire saw from the single crystal ingot thus obtained, and subjected to chamfering, lapping, etching, and mirror polishing. Then, silicon single crystal mirror polished wafer having a diameter of 6 inches were produced in almost the same condition except that nitrogen is doped or not, the cooling rate and the concentration of oxygen.

[0045] Measurement and comparison were performed through use of LST (Laser Scattering Tomography) as for the size of grown-in defect in the two resulting wafers one of which has the doped nitrogen concentration of  $0.2$  to  $5.0 \times 10^{15}$  atoms/cm<sup>3</sup> and the other has no doped nitrogen, and both of which were produced with a rate of cooling of  $2.3$  DEG C/min. The results were shown in Fig.1 and Fig.2. As shown in Fig.1 and Fig.2, among the resulting wafers obtained from the crystals having the same oxygen concentration of  $0.8 \times 10^{18}$  atoms/cm<sup>3</sup>, each of which was produced at a relatively high cooling rate as  $2.3$  DEG C/min, a size of a grown-in defect on the wafer obtained from the crystal without doping of nitrogen was about  $140$  nm (Fig.2), while a size of a grown-in defect on the wafer obtained from the crystal with doped nitrogen was about  $60$  nm (Fig.1). It is apparent that the latter is less than half of the former as a result of suppression of growth of defects.

[0046] The silicon single crystal wafer thus obtained was subjected to Secco etching, pit density was measured by observing the surface thereof with a microscope to determine a density of crystal defects (grown-in defects). The measurement was performed at a center portion, at a distance of a half of radius from the center, and at a peripheral portion of the wafers which were sliced from each of the single crystal ingots at a position of  $10$ ,  $20$ ,  $30$ ,  $40$ ,  $50$  or  $60$  cm from the shoulder part thereof.

[0047] The results were shown in Fig.3 to Fig.5. Fig. 3 is a graph showing a relation between an average value of crystal defect density of the silicon single crystal wafer sliced from the five silicon single crystal ingots in which nitrogen is doped and a rate of cooling. Fig.4 is a graph showing the defect density of the silicon single crystal wafer obtained from the ingot grown with doping nitrogen and with controlling a rate of cooling to be  $2.3$  DEG C/min. Fig.5 is a graph showing the defect density of the silicon single crystal wafer obtained from the conventional ingot grown without doping nitrogen. In each of the figures, square plots represent the data at the center of the wafer, circle plots represent the data at a distance of half of radius from the center of the wafer, triangle plots represent the data at peripheral part of the wafer.

[0048] As shown in Fig.3, as the cooling rate increases, the density of defect decreases. Therefore, it is apparent that the preferable cooling rate is  $2.3$  DEG C/min or more, especially,  $3.5$  DEG C/min or more. The reason for this can be considered that aggregation of the defect is suppressed at such a high cooling rate, and thus a size thereof decrease to be fine.

[0049] As shown in Fig.4, in production of the silicon single crystal wafer of the present invention, the pulling rate was  $1.0$  mm/min or more which was the same as or higher than that in a conventional method, nevertheless, the density of the crystal defects of all of the wafers sliced from the same crystal ingot was extremely decreased all over the wafer, to almost zero, in comparison with the wafer obtained by the conventional method. Namely, according to the present invention, there can be surely provided a silicon single crystal wafer having a density of crystal defects of  $40$  number/cm<sup>2</sup> or less on the surface of the wafer.

[0050] As shown in Fig.5, in the conventional silicon single crystal wafer, the density of the crystal defects tends to be higher in the wafer sliced from the farther part from the shoulder portion of the single crystal ingot. Particularly, the density of the crystal defects is  $600$  number/cm<sup>2</sup> or more in the wafer sliced from

the ingot at 20 cm far from the shoulder portion of the single crystal ingot.

[0051] The present invention is not limited to the above-described embodiment. The above-described embodiment is a mere example, and those having the substantially same structure as that described in the appended claims and providing the similar action and effects are included in the scope of the present invention.

[0052] For example, the method of the present invention can be applied not only for a Czochralski method but also for any type of MCZ method (Magnetic field applied Czochralski crystal growth method) in which magnetic field is applied when the silicon single crystal is pulled. Namely, the term "a Czochralski method" includes not only general Czochralski method but also MCZ method.

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**Claims**

1. A silicon single crystal wafer produced by processing a silicon single crystal ingot grown by Czochralski method with doping nitrogen, characterized in that a size of grown-in defects in the silicon single crystal wafer is 70 nm or less.
2. A silicon single crystal wafer produced by processing a silicon single crystal ingot grown by Czochralski method with doping nitrogen, characterized in that the silicon single crystal ingot is grown with controlling a rate of cooling from 1150 to 1080 DEG C to be 2.3 DEG C/min or more.
3. The silicon single crystal wafer according to Claim 1 or 2 characterized in that the nitrogen concentration in said silicon single crystal wafer is in the range of  $0.2$  to  $5 \times 10^{15}$  atoms/cm<sup>3</sup>.
4. The silicon single crystal wafer according to any one of Claims 1 to 3 characterized in that oxygen concentration in the single crystal wafer is  $1.0 \times 10^{18}$  atoms/cm<sup>3</sup> or less.
5. The silicon single crystal wafer according to any one of Claims 1 to 4 characterized in that the density of the crystal defects on the surface of the wafer is 40 number/cm<sup>2</sup> or less.
6. A method for producing a silicon single crystal wafer characterized in that a silicon single crystal ingot is grown with doping nitrogen and controlling a rate of cooling from 1150 to 1080 DEG C to be 2.3 DEG C/min or more, and is then processed to provide a silicon single crystal wafer.
7. The method for producing a silicon single crystal wafer according to Claim 6 characterized in that the nitrogen concentration doped in the single crystal ingot is  $0.2$  to  $5 \times 10^{15}$  atoms/cm<sup>3</sup>, when growing silicon single crystal ingot by Czochralski method with doping nitrogen.
8. The method for producing a silicon single crystal wafer according to Claim 6 or 7 characterized in that oxygen concentration in the single crystal ingot is  $1.0 \times 10^{18}$  atoms/cm<sup>3</sup> or less, when growing silicon single crystal ingot by Czochralski method with doping nitrogen.

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